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Effects of Aging Time on V_2O_5 Sol-Gel Coatings

by

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13. ABSTRACT (Maximum 200 words)

Vanadium pentoxide (V_2O_5) sols have been used in conductive coatings and related applications (1,2,3). From cryo-Transmission Electron Microscopy (TEM) and Nuclear Magnetic Resonance (NMR) spectroscopic studies of the gelation, there are several intermediate structures and reactions in this process (4,5,6), but no information is yet available on the effects of aging on the dependent properties of viscosity, conductance, and film morphology in the coating process. This study observed the changes in these properties over a 30 day period by means of rheological measurements and microscopic observation of the dried coatings obtained. The study found that the sol viscosity and ability to wet substrates is related to the initial decomposition of the precursors in solution and the start of the polymerization process. Distinct differences were observed in coating morphology as later aggregation and agglomeration processes occurred.

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EFFECTS OF AGING TIME ON V$_2$O$_5$ SOL-GEL COATINGS

(submitted to J. Noncrystalline Solids)

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ABSTRACT

Vanadium pentoxide (V_2O_5) sols have been used in conductive coatings and related applications[1,2,3]. From cryo-Transmission Electron Microscopy (TEM) and Nuclear Magnetic Resonance (NMR) spectroscopic studies of the gelation, there are several intermediate structures and reactions in this process[4,5,6], but no information is yet available on the effects of aging on the dependent properties of viscosity, conductance, and film morphology in the coating process. This study observed the changes in these properties over a 30 day period by means of rheological measurements and microscopic observation of the dried coatings obtained. The study found that the sol viscosity and ability to wet substrates is related to the initial decomposition of the precursors in solution and the start of the polymerization process. Distinct differences were observed in coating morphology as later aggregation and agglomeration processes occurred.

1. INTRODUCTION

Vanadium pentoxide gels exhibit a ribbon morphology in both solution and solid states[4,5,7,8]. The ribbon-like polymers have been measured to have dimensions of approximately 25nm x 3nm and over 1 micron in length in solution, and are transverse aggregations of linear polymers as shown by cryo-TEM microscopy[4,5]. NMR spectroscopic work has shown the ribbon polymerization follows a linear polymerization of the dioxovanadium cation, VO_2^+. Solutions after acidification have nearly 80% of the vanadium atoms incorporated into the decavanadic acid ($H_2V_{10}O_{28}^{4-}$) structure with the remainder present in the dioxovanadium cation[6]. More dioxovanadium cation is present than is needed for equilibrium with the decavanadic acid. However, the polymerization of VO_2^+ is much faster than the reaction to reform the decavanadic acid from this cation, so the polymerization to the ribbon structure will proceed while the decavanadic acid does not react initially. As the consumption of the dioxovanadium cation proceeds past that needed for equilibrium with the decavanadic acid, the decavanadic acid decomposes rapidly to the dioxovanadium cation monomer since the reaction to disassemble into the dioxovanadium cation is much quicker than that to reform from dioxovanadium cations. This attempt to re-establish equilibrium in the solution speeds the polymerization process which leads to a burst of amorphous particulate in solution, observed in several microscopic studies. It is this amorphous particulate that grows and forms the crystalline ribbon structure in solution[5]. The ribbon itself is a two-dimensional aggregation of linear entities as shown by the striations on the ribbon and observed fraying of the ribbon structure. The ribbon-like polymer exhibits a unit cell dimension of a=27.0 angstroms and b=3.6 angstroms in both solution and dried states[4,5,7,8], similar to a two-dimensional version of the vanadium pentoxide crystal. However, crystalline vanadium pentoxide does not exhibit the same conductivity as the dried vanadium pentoxide gel. These conductive properties lead to potential applications in switching devices, conductive coatings, micro-ionic devices and humidity sensors. A comprehensive review of the properties and applications of these gels is given in Reference 1. However, the relationship between the intermediate structures and reactions in solution and the quality of the coatings obtained during processing has not been fully addressed.

Reactions continue to occur as the solution ages, which could possibly change the characteristics of the sol and the applied coatings[6]. It is the effects on dried coating morphology and sol characteristics which has been examined in this work.

2. EXPERIMENTAL

V_2O_5 sols were made by the ion-exchange method with initial metavanadate salt concentrations of 0.1 to 0.2 M[8,9]. Low concentrations were chosen so that the effects of reaction and aging time could be easily examined. Viscosity changes of the reacting 0.1 M vanadate column effluent were monitored using a capillary viscometer with water as the standard reference. The sols were dip coated onto glass substrates.

Coatings were examined by Video Enhanced Microscopy (VEM) and Scanning Electron Microscopy (SEM). Conductivity measurements were made with an ohmmeter after coatings had dried.

3. RESULTS

After passing through the acid charged ion-exchange column, the acidified vanadate solution is light orange in color. Light orange-brown particles form in solution, and eventually span the volume of the container. The particles eventually form a viscous red gel. The time required for this color change to occur is approximately 5-7 days for 0.1M vanadate solutions.

Coatings applied prior to the formation of particles did not fully cover the substrate. Such coatings are spotty as the solution is unable to uniformly wet the surface of the substrate. A more uniform coverage is achieved as the 0.1M vanadate solution approachs the 7 day change in color.

The thickness of the coatings applied to the substrate were measured using VEM. The coatings applied at day 1 showed only a spotty coverage with a maximum thickness of 3 microns. At days 3 and 4, the surface of the coated substrate is still sparsely covered with a minimum thickness of zero, but the maximum thicknesses have increased to 10 microns at day 3 and from 15 to 20 microns at day 4. After day 6, the coating uniformly covers the substrate with an average

thickness of 20 microns. However, at day 14, outcroppings of maximum thicknesses of 40 to 50 microns are achieved.

As a uniform coverage is achieved on the surface of the substrate, several sol and film properties change. As the red sol evolves, Figure 1 shows that the viscosity increases from 1 to 2 centipoise at 5-7 days as the solution changes from a particulate suspension in water to a homogeneous sol. The viscosity continues to increase, but at a much slower rate. Sols at this vanadate concentration never form a solid gel but remain a slightly viscous liquid, so the viscosity may eventually reach an asymtotic value.

The conductance of the coatings also demonstrates a noticeable increase as shown in Figure 2. After the initial increase, there is no noticeable change in the conductance. Using the thicknesses measured, the approximate range of conductivity for the dried gel is 2.0 to 3.0 x 10^{-4} $(ohm*cm)^{-1}$ for all coatings measured. This is slightly above the conductivity observed for xerogels obtained from ion-exchanged sols, which has been reported to be 10^{-5} $(ohm*cm)^{-1}$[8].

The X-ray diffraction patterns of the dried coatings show the development of the well documented lamellar structure of the xerogel, which gives diffraction peaks at 00m intervals[14]. The diffraction patterns for days 2, 4, 6, and 8 are shown on Figure 3. The diffraction peaks at 001 and 003 are observed on all coatings, but the 004 peak is not observed on all diffraction patterns. The 001 and 003 peaks are also observed to shift nearly one-half degree from day one to day six. This may not be significant due to the insufficient coverage and low thicknesses of the coatings obtained at these days. The peaks also become substantially less broad and more intense from day one to eight, after which no further change in the diffraction patterns are seen.

The evolving surface structure of the dried coating was also followed using VEM and SEM. Figure 4 shows a VEM sequence of the structure evolution from a grainy surface where no structure is evident to an eventual uniform coverage of rough, wavy micron-sized structures. A higher resolution SEM sequence shown on Figure 5 was obtained for dried coatings obtained from a 0.2M vanadate solution aged for 5 days and then for 8 days. Color change was achieved prior to the 5 day application. At five days, the structure on the surface is just starting to form and resembles bunches of string-like structures just starting to aggregate. At eight days, the morphology of the surface resembes a homogeneous mass of micron-sized rope-like masses.

4. DISCUSSION

The increase in viscosity occurs after the induction time previously observed[5,6]. This increase in viscosity at days 5 to 7 leads to a better overall coverage on the coated substrates and increased coating thickness as the ability of the reacting solution to wet the substrate improves. The viscosity increase also occurs after the burst of amorphous particles and initial rapid decomposition of the decavanadic acid[5,6]. Viscosity of the sol increases less rapidly beyond day 7 as the reactions in solution slow due to the lowered concentrations of the initial dissolved precursors in solution. The viscosity may reach a final value as the remainder of the reactants are consumed and a definite volume fraction of the solution becomes occuppied by the entangled ribbon polymers.

The conductance of the coatings shows an increase that can be accounted for by the improved coverage on the substrates as the viscosity increases. The conductivity differences from those sited in literature can be accounted for by the dependence of the conductivity on humidity conditions in the laboratory which has been a source of variance in previous measurements[10,11]. The amount of vanadium(IV) is also higher in these sols, near 1% of the total vanadium concentration, which is could be another source of the conductivity increase[6,12,13].

The X-ray diffraction patterns for the evolving coatings show more definition as the thickness of the coating improves, but does not differ significantly from those patterns noted previously[14]. This is an effect of the improved ability of the sol to wet the substrate. The new observeable peak at 004 is an indication that the sol has completed the assembly into the ribbon polymer which then stacks into the characteristic lamellar structure during drying.

The VEM and SEM sequences of the evolving coatings also show a dependence on reaction time. The coatings show that although the linear ribbon-like nature of the sol has been achieved there are differing degrees of aggregation occuring during the gelation process. The initial coatings show a "grainy" appearance that corresponds to an abscence of structure formation. This can be related to the abscence of the ribbon polymers in the coating sols at this time. Microscopy studies studies show blank fields at this time in the reaction process[5]. After formation

of the ribbon polymers, the micrographs in Figures 4b & 4c show the formation of micron-sized structures on the coating. The first SEM micrograph in Figure 5a shows the initial formation of the coating with masses of aggregated ribbons still visible. The later micrograph, Figure 5b, shows the larger resulting aggregation of thread-like polymers into micron-sized "ropes" on the surface of the coating.

The amount of aggregation of ribbon polymers appears to be a further factor in the surface morphology of the coatings in addition to the initial ribbon formation. The early microscopic studies of the gelation in this system utilized the birefringent nature of this material and used polarized light to illuminate the structures forming in solution[15,16]. These studies have shown blank fields in the microscope after acidification, but as the reactions proceed, tactoids, or ellipsoidal structures with the characteristic maltese cross, are observed to form[15,16]. Detailed characterization and studies of this structure have already been done[17].

The initial appearance of the birefringent tactoid structures would correspond to the first microscopic masses of ribbons that start to aggregate in solution[5]. These birefringent structures are 40-70 microns in size. The images obtained from the aged sols in this study contained tactoids that were only 20-30 microns in size and were more circular in shape. These tactoids were most often found in large aggregations, or clusters, as shown in Figure 6. This illustrates that the later steps of the gelation process after the initial ribbon formation and aggregation are controlled by further agglomeration of the masses of ribbons in solution into the clusters seen in Figure 6. It is these larger agglomerates that cause the formation of the large micron-sized "ropes" on the coating surface of Figure 5b. This view of the latter end of the gelation process where the tactoidal structures agglomerate to form the gel has previously been advanced by early researchers in this field[17]. Although there are distinct differences in surface morphology from the dried coatings, there is no noticeable change in conductance of the dried coatings as seen from Figure 2. However, the surface morphology of the coatings may have important consequences in the area of electrical contacts for conductive applications.

5. CONCLUSIONS

From the micrographs of the surface morphology, definite surface structure changes can be achieved by coating V_2O_5 sols at different times in the aging process, which coincide with the different distinct steps in the gelation process. Increases in solution viscosity and improved film thickness occur which coincide with the ribbon polymerization process and color change of the reacting solution. Changes in surface morphology occur which coincide with the aggregation of ribbon polymers and the later agglomeration of the ribbon aggregates. Optimum coating conditions can be predicted by relations between the rate of growth of colloids and the resultant increase in viscosity and coating thickness.

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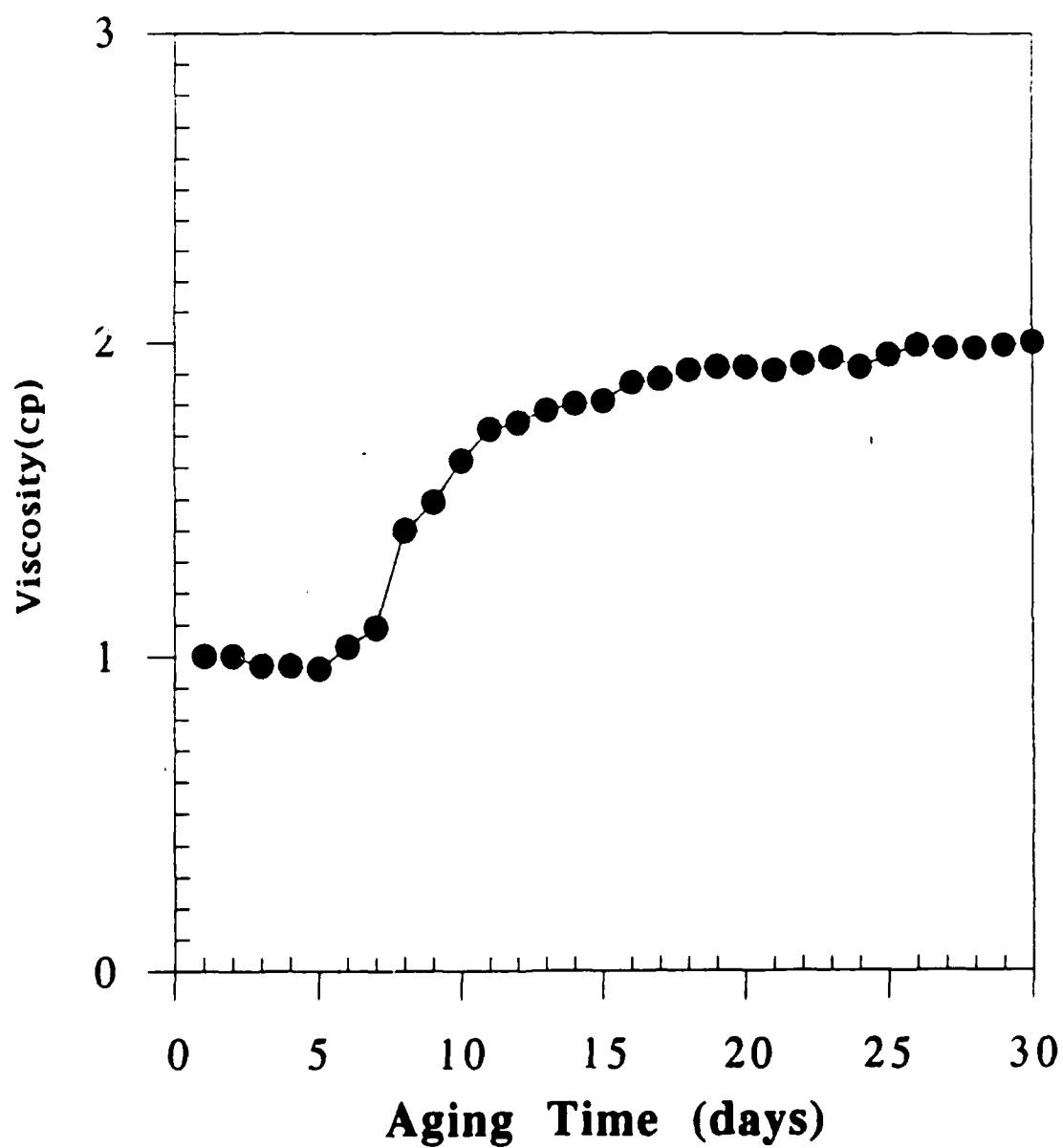
Figure 1. Viscosity vs Aging Time
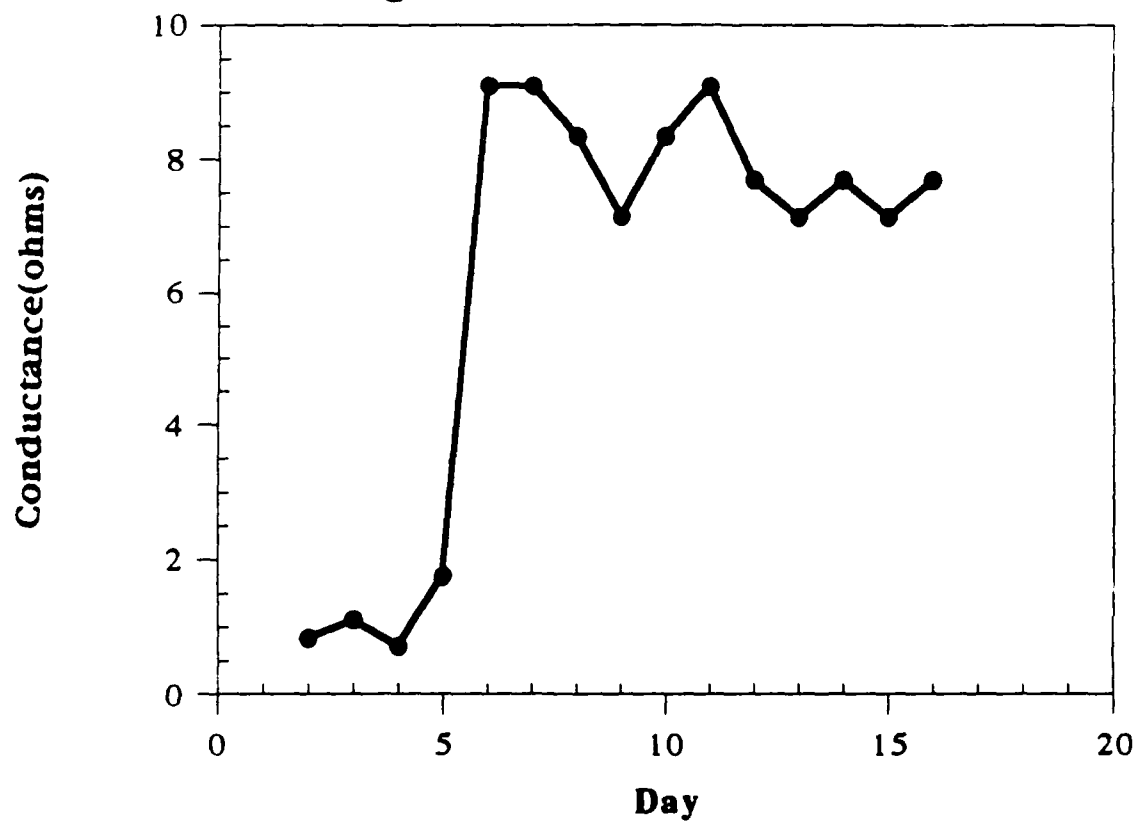
Figure 2. Conductance vs. Time

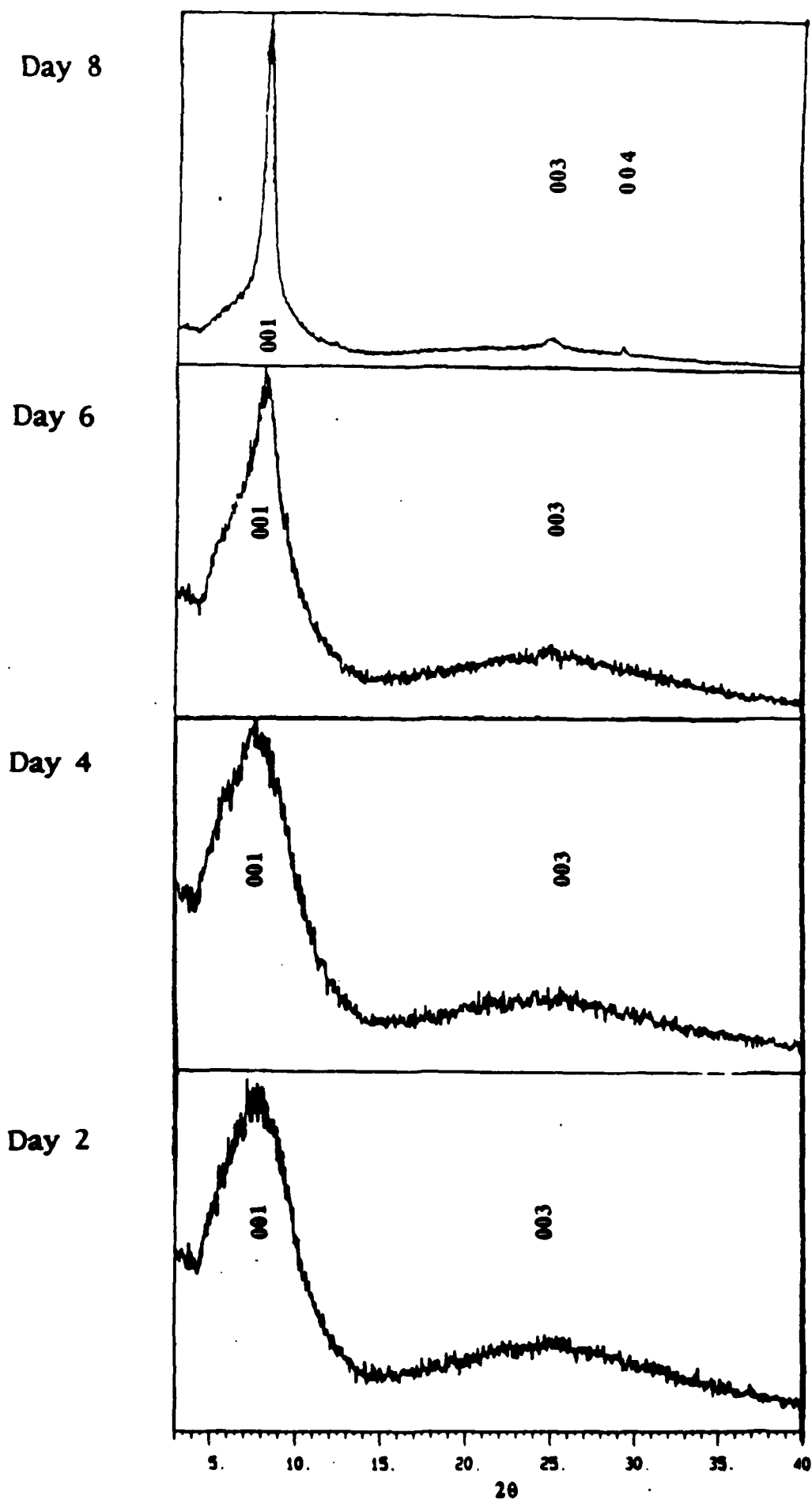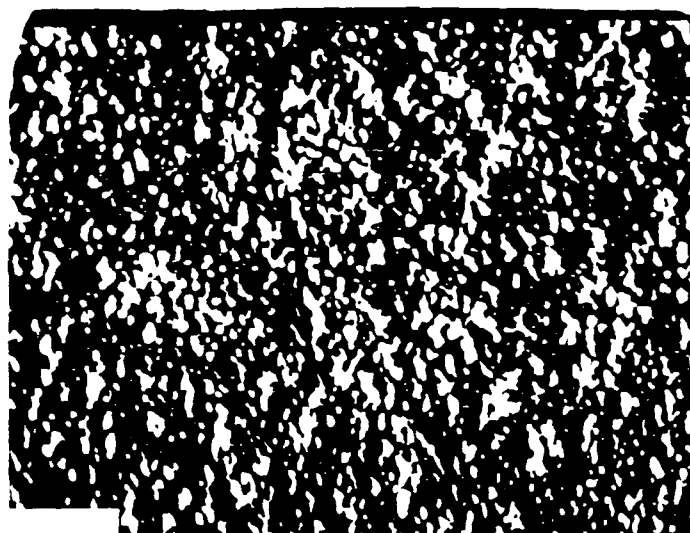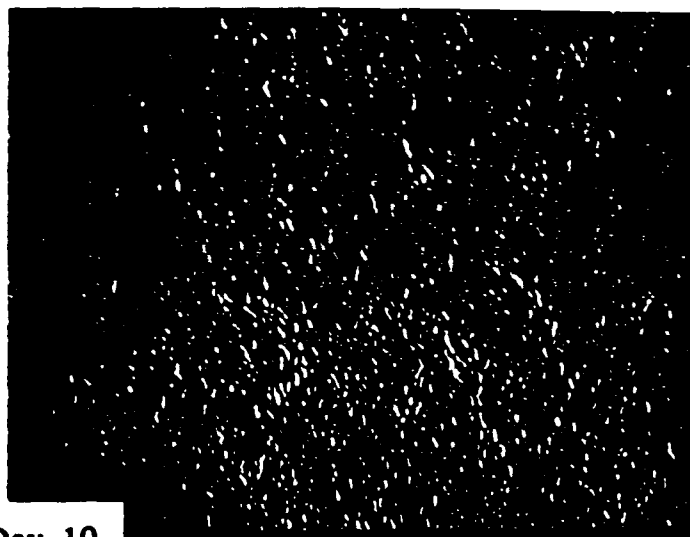Figure 3. X-Ray Diffraction Patterns for Days 2, 4, 6 and 8

Figure 4. VEM Sequence of Coated Surfaces

Figure 4a.

Day 7

Figure 4b.

Day 10

Figure 4c.

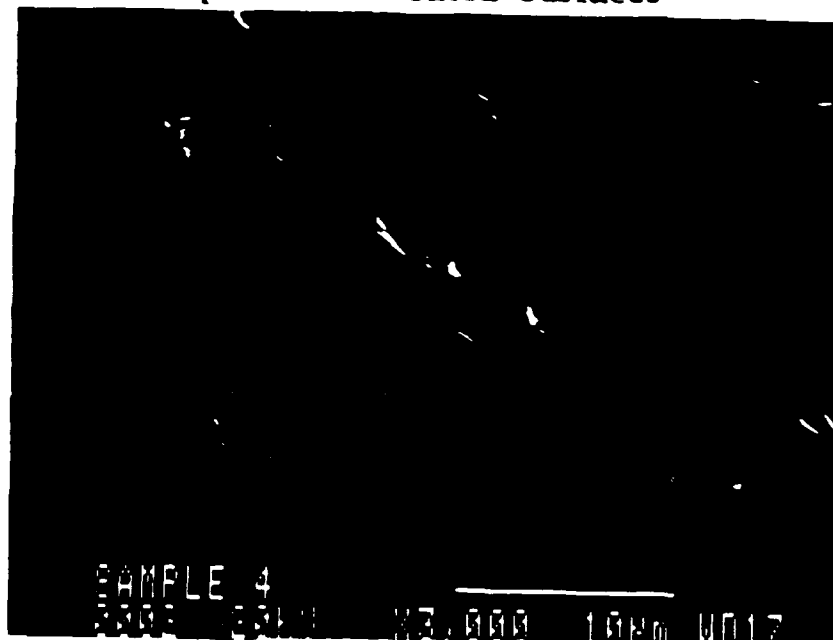Day 21

10 microns

Figure 5. SEM Sequence of Coated Surfaces
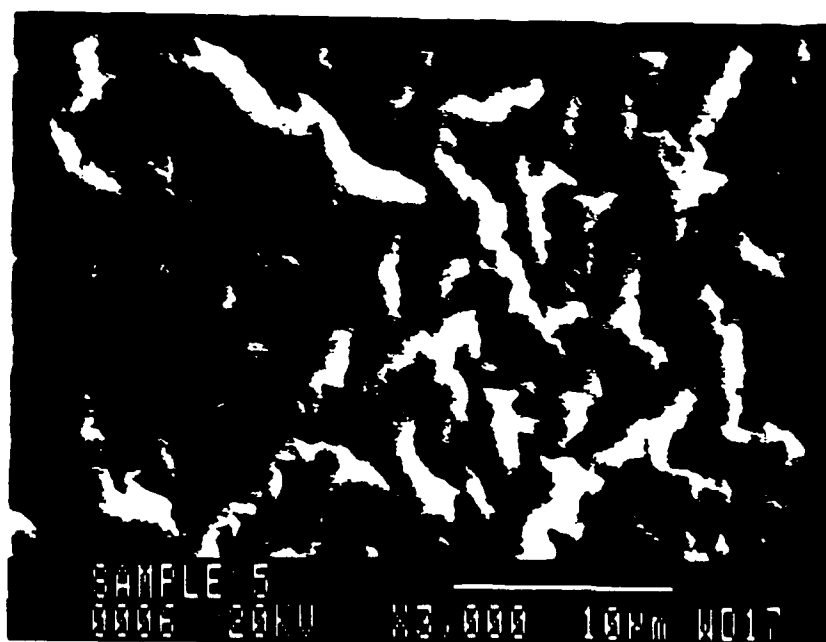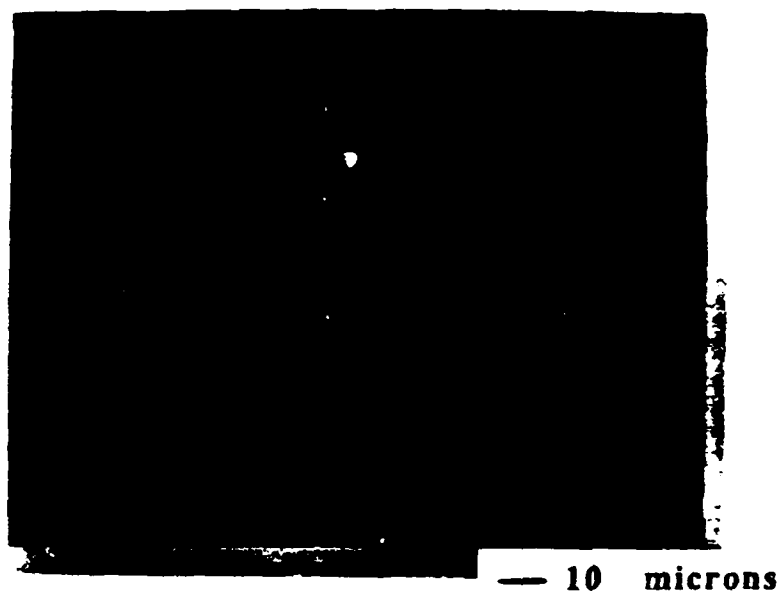

Figure 5a. 5 days

Figure 5b. 8 days

Figure 6. Polarized Light Image of Tactoidal Cluster

— 10 microns

Figure 6.   Polarized Light Image of Tactoidal Cluster

— 10   microns